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Synthesis and application of a new selenoplatinum catalyst

Pavel Arsenyan,* Kristine Oberte, Kira Rubina and Sergey Belyakov

Latvian Institute of Organic Synthesis, Aizkraukles 21, Riga, LV 1006, Latvia

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Abstract—The reaction of 4-methyl-5-ethoxycarbonyl-1,2,3-selenadiazole with $(PPh_3)_4Pt$ leads to the formation of a new platinum-containing heterocyclic system. It was found that the selenoplatinum complex is a selective catalyst for the hydrosilylation of terminal alkynes to yield β-(*Z*)- and β-(*E*)-silylethylenes.

Recently, the syntheses and use of selenium-containing compounds in organic synthesis has increased.[1] The interest in 1,2,3-selenadiazoles stems from the fact that they undergo a wide variety of reactions as 1,3-dipoles or as a source of selenium and have attracted much attention for the synthesis of different organoselenium compounds. The reactions of 1,2,3-selenadiazoles with low-valent transition metal compounds have previously been used to prepare a variety of selenium-containing complexes. Reaction of cyclohepteno-1,2,3-selenadiazole with a two fold excess of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ leads to the formation of a dimolybdenum complex in 10% yield.[2] It has been shown that cyclopentadienylcobalt diselenolenes may be produced by interaction of di(triphenylphosphino)- or dicarbonylcyclopentadienyl cobalt(0) with 4,5-disubstituted 1,2,3-selenadiazoles in the presence of elemental selenium.[3a,b] Diiron diselenolates have been synthesized using nanocarbonyldiiron.[3c] Heating $Pd_2(dba)_3$ and 1,2,3-selenadiazoles with 1 equiv of trialkylphosphine led to the formation of a complex containing Se, N, Se tridentate ligands.[4a,b] A selenaketocarbene complex containing platinum was obtained from cyclooctено-1,2,3-selenadiazole and tetrakis(triphenylphosphino)platinum(0) in high yield.[4c]

We now present a totally new type of platinum complex prepared from 4-methyl-5-ethoxycarbonyl-1,2,3-selenadiazole and tetrakis(triphenylphosphino)platinum(0). The catalytic application of this selenoplatinum complex was studied for the hydrosilylation of terminal acetylenes with phenyldimethylsilane. The new catalyst enables the synthesis of previously unknown β-(*Z*)-silylethylenes.

The reaction of 4-methyl-5-ethoxycarbonyl-1,2,3-selenadiazole (**1**)[5] with 1 equiv of tetrakis(triphenylphosphino)platinum(0) in toluene at 140 °C in a Pierce vial for 3 h led to the formation of a new platinum-containing heterocyclic system. This reaction involved the insertion of di(triphenylphosphino)platinum into the selenadiazole ring yielding the six-membered ring **2**. During the second step a 1,3-dipole formed from selenadiazole **1** by thermal elimination of nitrogen adds to intermediate **2** with the elimination of triphenylphosphine to yield the new heterocycle **3**.[6] The platinum is covalently bonded to two selenium atoms and has an intramolecular donor–acceptor bond with nitrogen, and a coordinate bond with triphenylphosphine (Scheme 1). Compound **3** was obtained in 35% yield as dark-violet crystals after recrystallization from hexane. Previously palladium-containing heterocycles with similar structures were prepared by Morley and coworkers in 1999.[4b] The desired product was formed from the selenadiazole and $(PPh_3)_4Pd$ at 60 °C in benzene after 1 h and in low yield. In our case the molecular structure of selenoplatinum heterocycle **3** was established by X-ray analysis.[7] The atomic labeling and the ORTEP view of **3** is presented in Figure 1. The Pt1–Se2 bond length in the six-membered ring (2.345 Å) is shorter than the Pt1–Se9 bond length in the five-membered ring (2.394 Å). Heterocycle **3** is stabilized by the triphenylphosphine ligand, the Pt1–P10 bond length is 2.259 Å, and the intramolecular Pt1–N6 bond is 2.079 Å. The bond lengths in **3** are in accord with Pt–Se

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* Corresponding author. Tel.: +371 753 1028; fax: +371 755 0338; e-mail: pavel.arsenyan@lycos.com

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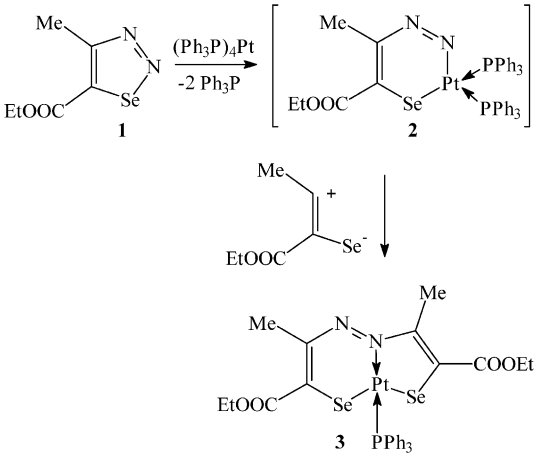


Scheme 1. Interaction of 4-methyl-5-ethoxycarbonyl-1,2,3-selenadiazole **1** with tetrakis(triphenylphosphino)platinum(0).

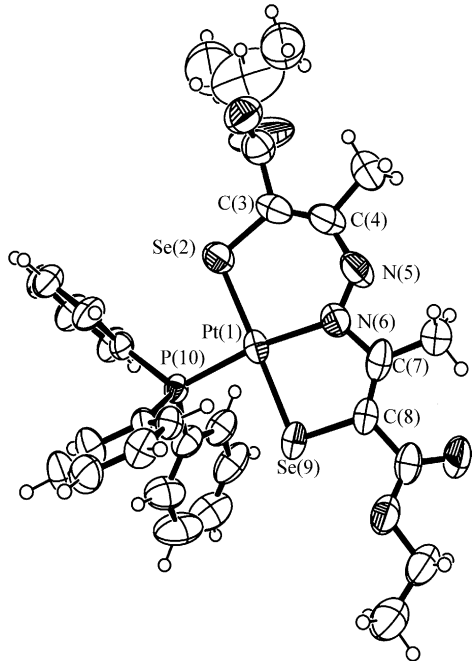


Figure 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Pt1–Se2 2.3448(7), Pt1–Se9 2.3941(7), Pt1–P10 2.2596(12), Pt1–N6 2.071(5), Se9–C8 1.859(5), Se2–C3 1.836(6), N6–C8 2.323(7), N6–C7 1.434(8), N6–N5 1.295(7), N6–C4 2.398(8), C8–C7 1.322(9), C7–N5 2.189(9), N5–C4 1.420(9), Se9–Pt1–Se2 176.48(3), Se9–Pt1–P10 87.61(3), Se9–Pt1–N6 82.93(13), Se2–Pt1–P10 90.83(4), Se2–Pt1–N6 98.73(13), P10–Pt1–N6 170.33(14), Pt1–Se9–C8 95.4(2), Pt1–Se2–C3 103.6(2), Pt1–N6–C8 92.0(2), Pt1–N6–C7 123.0(4), Pt1–N6–N5 130.4(5), Pt1–N6–C4 101.0(3).

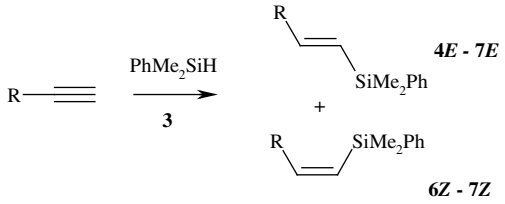
(2.377–2.479 Å) and Pt–P (2.229–2.305 Å) bond distances of previously published structures.[8] The Se2–Pt1–Se9 angle is almost linear (176.48°). The methyl groups of the ethoxycarbonyl substituent at C3 appear disordered in the crystal structure.

According to literature data[9a] the hydrosilylation of trichloro(ethynyl)silane with trichloro-, dimethylchloro-, and trimethylsilanes in the presence of Speier's catalyst yields two β-(*E*)- and α-silylethylenes. However, hydrosilylation of alkylalkoxyethynylsilanes with chloroalkylsilanes catalyzed by $H_2PtCl_6{\cdot}6H_2O$ gives only the β-(*E*)-isomer.[9b,c] In the synthesis of methylarylsilanes, the hydrosilylation reaction predominantly forms the β-(*E*)-ethylene, which in the case of ethynylsilatrane is the only product (Table 1).[9d,e] Hydrosilylation in the presence of rhodium catalysts occurs less selectively to afford both the hydrosilylation products and the products of a dehydrocondensation. It should be noted that the β-(*Z*)-isomer was not obtained in the previously described experiments.

We have found that the new selenoplatinum complex **3** can catalyze the hydrosilylation of *tert*- butyl-, trimethylsilyl-, phenyl-, and methoxycarbonyl substituted acetylenes with dimethylphenylsilane in good yields (74–80%). 3,3-Dimethylbut-1-yne reacts with dimethylphenylsilane at 50 °C in 2 h and in 80% yield almost stereospecifically to give the β-(*E*)-isomer **4***E* with only traces of the *Z*-isomer. In the case of trimethylsilylacetylene, hydrosilylation also occurred stereospecifically to give β-(*E*)-1-trimethylsilyl-2-dimethylphenylsilylethylene (**5***E*). In contrast the use of Speier's catalyst gave a regioisomeric ratio of 96% (**5***E*) to 4% (the α-isomer).[9e] Reaction of the silane with phenylacetylene led to the formation of a stereoisomeric mixture. β-(*E*)-2-Dimethylphenylsilylstyrene (**6***E*) was obtained in 75% yield as the major product along with the β-(*Z*)-isomer **6***Z* in 25% yield. According to ^{1}H NMR spectroscopy the alkene double bond protons of **6***Z* appeared as doublets at 5.65 and 5.98 ppm ($^3J = 3.0$ Hz). Inspection of the literature data showed that no platinum catalysts had previously been reported for the synthesis of β-(*Z*)-isomers by hydrosilylation. Analysis of the product mixture after hydrosilylation of methyl propiolate showed that methyl β-(*Z*)-2-dimethylphenylsilylacrylate **7***Z* was formed in a small excess in comparison to the **7***E* isomer.[10] It should be noted that selenoplatinum catalyst **3** can be almost quantitatively recovered from the reaction mixture by column chromatography on silica gel and reused more than five times (Scheme 2).

Table 1. Addition of dimethylphenylsilane to terminal acetylenes

R	**3** Regioisomer ratio (%)			Yield (%)	$[H_2PtCl_6]$[9d,e] Regioisomer ratio (%)		
	α	β-(*E*)	β-(*Z*)		α	β-(*E*)	β-(*Z*)
^{t}Bu	—	4*E* 99	Traces	80	4	96	—
Me_3Si	—	5*E* 99	Traces	74	24	76	—
Ph	—	6*E* 75	6*Z* 25	79	31	69	—
COOMe	—	7*E* 45	7*Z* 55	76	60	40	—



Scheme 2. Hydrosilylation of terminal acetylenes with dimethylphenylsilane in the presence of catalyst **3**.

Despite the reports on the platinum catalysts of Karstedt et al. and Lewis et al.[11] our attempts to use catalyst **3** in the hydrosilylation of vinylsilanes with phenyldimethylsilane failed.

In summary, we have presented a method for the synthesis of a new type of platinum heterocycle and it crystal structure. It was found that the selenoplatinum compound acted as a selective catalyst in hydrosilylation reactions to yield β-(*Z*)- and β-(*E*)-silylethylenes.

Acknowledgements

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6. General procedure for the synthesis of 3,5-dimethyl-1,7-diselena-3a,4-diaza-7a-triphenylphosphino-7a-platinaindene-2,6-dicarboxylic acid diethyl ester (**3**): Selenadiazole **1** (0.05 mmol) and tetrakis(triphenylphosphino)platinum (0.05 mmol) were dissolved in 5 mL of toluene. The reaction mixture was heated at 130 °C for 1 h. The solvent was evaporated and the residue purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:5, $R_f = 0.60$), mp = 210–212 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): 1.22 (3H, t, $J = 6.5$ Hz), 1.29 (3H, t, $J = 6.5$ Hz), 2.78 (3H, s), 2.90 (3H, s), 4.35 (2H, q, $J = 6.5$ Hz), 4.38 (2H, q, $J = 6.5$ Hz), 7.45–7.74 (15H, arom). ^{13}C NMR (50.31 MHz, $CDCl_3$, 298 K): 13.6, 14.4, 24.9, 25.5, 61.6, 62.0, 128.0, 128.2, 128.7, 131.5, 135.1, 135.4, 165.8, 166.2. Anal. Calcd for $C_{30}H_{31}N_2O_4PPtSe_2$: C, 41.53; H, 3.60; N, 3.23. Found: C, 41.42; H, 3.58; N, 3.26.
7. Single-crystal X-ray diffraction: Nonius KappaCCD difractometer (Mo Kα-radiation, $\lambda = 0.71073$ Å; $T = 293(2)$ K). The structure was solved by direct methods (SIR-97, Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115) and refined by FMLS on F^2 (Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Göttingen (Germany), 1997) in anisotropic approximation. Hydrogen atoms were refined by the riding model. $C_{30}H_{31}N_2O_4PPtSe_2$, $M_r = 867.55$, dark-violet crystals, $0.10 \times 0.11 \times 0.26$ mm; monoclinic, space group $P2_1/c$ (No 14); $a = 9.2592(1)$, $b = 15.5252(3)$, $c = 23.8922(5)$ Å, $\beta = 110.609(1)°$, $V = 3214.7(1)$ Å^3; $Z = 4$; $\mu = 6.715$ mm^{-1}; $\rho_{calcd} = 1.792$ g cm^{-3}; 15535 reflections ($2\theta_{max} = 60°$), 9289 unique ($R_{int} = 0.034$), 360 parameters; largest max/min in final difference Fourier synthesis: 6.113 e Å^{-3} (0.807 Å from Pt atom)/ −3.904 e Å^{-3} max/min transmission 0.5532/0.2742; $R = 0.078$ (for 6386 reflections with $I > 2\sigma(I)$), wR (on F^2) = 0.172. CCDC-233367 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.acm.ac.uk/conts/retrieving.html.
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10. General procedure for the hydrosilylation reactions: The reactions were conducted in Pierce reactors at 80 °C. A mixture of hydrosilane (0.5 mmol), terminal acetylene (0.5 mmol) and catalyst **3** (1×10^{-6} mol) was heated for 2 h. The ratio of isomers was determined on the basis of GC–MS and ^{1}H NMR spectra. β-(*E*)-2-Dimethylphenylsilylstyrene (**6***E*). GC–MS (*m*/*z*): 238 [$M^{+\cdot}$] (32), 223 [$M^{+\cdot}-CH_3$] (39), 207 [$M^{+\cdot}-2\ CH_3$] (5), 197 (15), 145 (24), 135 [$M^{+\cdot}-PhCH{=}CH$] (100), 105 (20). ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): 0.26 (6H, s), 5.65 (1H, d, $J = 3.0$ Hz), 5.98 (1H, d, $J = 3.0$ Hz), 7.29–7.55 (10H, arom). Methyl β-(*Z*)-2-phenyldimethylsilylacrylate (**7***Z*). GC–MS (*m*/*z*): 220 [$M^{+\cdot}$] (5), 205 [$M^{+\cdot}-CH_3$] (100), 189 (15), 175 (57), 151 (84), 143 (40), 135 [$M^{+\cdot}-CH{=}CHCOOMe$] (45), 121 (40). ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): 0.41 (6H, s), 3.69 (3H, s), 5.97 (1H, d, $J = 3.2$ Hz), 6.85 (1H, d, $J = 3.2$ Hz), 7.32–7.38 (3H, arom), 7.46–7.55 (2H, arom).
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